

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 157 741 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

28.11.2001 Bulletin 2001/48

(51) Int Cl.7: **B01J 35/00**

(21) Application number: 01116337.5

(22) Date of filing: 23.06.1994

(84) Designated Contracting States:

AT BE CH DE DK ES FR GB GR IE IT LI LU MC NL
PT SE

(30) Priority: 28.06.1993 JP 18183493

26.10.1993 JP 29121293

(62) Document number(s) of the earlier application(s) in
accordance with Art. 76 EPC:

98111372.3 / 0 875 289

94109759.4 / 0 633 064

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Remarks:

This application was filed on 05 - 07 - 2001 as a
divisional application to the application mentioned
under INID code 62.

(54) **Photocatalyst composite and process for producing the same**

(57) A photocatalyst composite is provided which
comprises a substrate having a first adhesive layer free
of particles with photocatalytic function and a second
layer containing particles of a photocatalyst such as ti-
tanium oxide, adhered thereon via a less degradative

adhesive such as a fluorinated polymer comprising a co-
polymer of a vinyl ester and/or a vinyl ether and a
fluoroolefin.

Furthermore, a process for producing the photocat-
alyst composite and a coating composition containing
the photocatalyst composite are provided.

Description

[0001] The present invention relates to a photocatalyst composite comprising a substrate having photocatalyst particles adhered thereon and a process for producing the same.

DESCRIPTION OF RELATED ART

[0002] Exposure of photocatalyst particles to an irradiation of a wavelength corresponding to not less than the band gap energy causes the photoexcitation of electrons into a conduction band with a corresponding generation of holes in a valence band. The strong reduction power of the electrons and the strong oxidation power of the holes generated by this optical excitation have been utilized in decomposition and purification of organic materials as well as in decomposition of water. The photocatalyst particles to be used in such treatments are usually deposited on a substrate of dimensions larger than the photocatalyst particles in order to prevent them from scattering into the air or exhausting out of the system and subsequently to provide for easy separation of the photocatalyst from the treatment system. The deposition of photocatalyst particles on a substrate has been accomplished by a method comprising sintering the photocatalyst particles on the substrate at a temperature of 400 °C or higher to adhere the particles to the substrate, or a method comprising spraying a precursor, which can be converted to photocatalyst through thermal decomposition, onto a substrate heated at a temperature of about 400°C, thereby adhering the particles on the substrate. Alternatively, there has been proposed a method immobilizing photocatalyst particles using a certain type of fluorinated polymer. For example, Japanese Patent KOKAI (Laid-open) No. Hei 4-284851 discloses a photocatalyst consisting of a porous Ni base which had been coated with a mixture of photocatalyst particles and a fluorinated polymer by compressing the laminate under a pressure. It is said that the photocatalyst particles are effectively fixed on the porous Ni base by the action of the fluorinated polymer. Japanese Patent KOKAI (Laid-open) No. Hei 4-334552 discloses a method comprising thermally fusing a fluorinated polymer to adhere photocatalyst particles thereto.

[0003] JP-A-5-146671 discloses a process for optically immobilizing carbon dioxide, characterized by producing an oxygen-containing hydrocarbon, by bringing carbon dioxide and water under irradiation of a ray into contact with a photocatalyst composite comprising light-transmitting porous inorganic particles having an oxide semiconductor carried thereon thermally fused with a light-transmitting fluororesin onto a light-emitting porous substrate.

[0004] Recently, an attempt has been made to use photocatalyst particles for decomposition of deleterious materials, malodorous materials and oily substances in the waste products produced daily in inhabitant circumstances as well as purification and sterilization of the waste products. Thus the photocatalyst particles have found ever broadening areas of application. In this regard, there is a need for a method capable of adhering firmly photocatalyst particles onto any substrate, which adhesion can be maintained over an extended period of time, without losing their photocatalytic function.

[0005] Unfortunately, the prior art methods as described above suffer from insufficient adhesion strength as being susceptible to delamination under external pressure, and they require heating at high temperatures so that they can not apply to a substrate not resistant to heat such as plastics, interior materials such as office walls and the surfaces of various products which are difficult to heat, and the like. In addition, there are problems that the thermal treatments at high temperatures cause the photocatalyst particles to reduce their specific surface area resulting in a reduction in their photocatalytic function. Moreover, there may be required specific means such as devices for adhering under pressure, or fusing under heat.

SUMMARY OF THE INVENTION

[0006] One object of the present invention is to provide a photocatalyst composite comprising a substrate having photocatalyst particles adhered thereon via a less degradative adhesive.

[0007] Another object of the present invention is to provide a process for producing the photocatalyst composite.

[0008] A further object of the present invention is to provide a coating composition using the photocatalyst composite.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0009] The present inventors have made a research to develop a process for achieving a firm adhesion of photocatalyst particles onto any substrate over an extended period of time without damaging the photocatalytic function of the particles. As a result, the present invention has been completed on the basis of the discovery that (1) when photocatalyst particles are adhered onto a substrate with an adhesive, the photocatalytic function of the photocatalyst particles may decompose and deteriorate the adhesive causing the photocatalyst particles to release from the substrate, and however, the use of a less degradative adhesive and providing the substrate with a first adhesive layer without photocatalyst particles allow adhesion of the photocatalyst particles onto any substrate without causing the release of the particles

therefrom and unpredictably the photocatalyst of the present invention to exhibit sufficient photocatalytic function, (2) the photocatalyst particles may be adhered to a substrate without lowering the photocatalytic function of the resultant photocatalyst composite when the amount of the photocatalyst particles is in the range of 5 to 98 % based on the total volume of the photocatalyst particles and the less degradative adhesive, (3) the use of fluorinated polymers as less degradative adhesives results in most reduced decomposition and degradation of the adhesives owing to the photocatalytic function of the photocatalyst particles so that the photocatalyst particles can be firmly adhered for a long time, wherein as fluorinated polymers copolymers of vinyl ethers and/or vinyl esters and fluoroolefins are preferred, (4) preferred photocatalyst particles are titanium oxide which has a high photocatalytic function, a high chemical stability and no toxicity, and that (5) the process for producing a photocatalyst composite by disposing photocatalyst particles and an adhesive on a substrate and then solidifying the adhesive to adhere the photocatalyst particles via the adhesive, said process also comprises the steps of providing a first layer of an adhesive free from photocatalyst particles on a substrate by coating or spraying said substrate with said adhesive and fixing said adhesive onto said substrate, and the providing a second layer comprising a less degradative adhesive and then photocatalyst particles on said first layer and then fixing said adhesive and photocatalyst particles on said first layer, said less degradative adhesive being one or more polymers selected from the group consisting of a fluorinated polymer.

[0010] With other words the present invention provides a photocatalyst composite comprising any substrate having photocatalyst particles firmly adhered thereon for an extended period of time without losing the photocatalytic function of the particles.

[0011] As used in the present invention, the term "less degradative adhesive" refers to an adhesive having an extremely reduced rate of decomposition due to the photocatalytic function possessed by the photocatalyst particles in the range of 10 % or less, preferably 5 % or less, more preferably 3 % or less, most preferably 1 % or less expressed as a weight loss of the adhesive in the photocatalyst composite as measured by the method described in the Example below. A weight loss higher than 10 % indicates undesirably vigorous decomposition or degradation of the adhesive with a great amount of the photocatalyst particles being released.

[0012] These adhesives may be used in combination of two or more thereof.

[0013] The fluorinated polymers to be used include, for example, crystalline fluorinated resins such as polyvinyl fluorides, polyvinylidene fluorides, polyethylene trifluorochlorides, polyethylene tetrafluorides, tetrafluoroethylenehexafluoropropylene copolymers, ethylene-polyethylene tetrafluoride copolymers, ethylene-ethylene trifluorochloride copolymers, tetrafluoroethyleneperfluoroalkylvinyl ether copolymers, amorphous fluorinated resins such as perfluorocyclo polymers, vinyl ether-fluoroolefin copolymers, vinyl ester-fluoroolefin copolymers and various fluorinated elastomers. Particularly fluorinated polymers comprising primarily vinyl ether-fluoroolefin copolymers and vinyl ester-fluoroolefin copolymers are preferred because they are susceptible to less decomposition and degradation and easy to handle.

[0014] As used in the present invention, the term "photocatalyst particles" refers to those capable of exhibiting photocatalytic function upon irradiation with a radiation having a wavelength corresponding to not less than the band gap energy. The photocatalyst particles to be used include one or a combination of two or more of known metal compound semiconductors such as titanium oxide, zinc oxide, tungsten oxide, iron oxide, strontium titanate, and the like. Particularly titanium oxide which has a high photocatalytic function, a high chemical stability and no toxicity is preferred. In addition, it is preferred to include inside said photocatalyst particles and/or on the surfaces thereof at least one metal and/or a compound thereof selected from the group consisting of V, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Pt and Au as a second component because of the higher photocatalytic function of the resulting photocatalyst particles. The aforementioned metal compounds include, for example, metal oxides, hydroxides, oxyhydroxides, sulfates, halides, nitrates, and even metal ions. The content of the second component may vary depending upon the kind thereof. Preferred photocatalyst particles which may contain the aforementioned metals and/or metal compounds are of titanium oxide. The content of photocatalyst particles is preferably in the range of 5 to 98 % by volume based on the total amount of the photocatalyst particles and the less degradative adhesive. The content of the photocatalyst particles less than the above defined range tends undesirably to result in a reduced photocatalytic function of the resulting photocatalyst, while that higher than the above defined range tends also undesirably to cause a reduction in adhesion strength. When the fluorinated polymers are used as less degradative adhesives, the content of the photocatalyst particles should be preferably from 20 to 98 %, more preferably 50 to 98 % and most preferably 70 to 98 %.

[0015] The photocatalyst particles to be used in the present invention may be produced by any one of known techniques. For example, there are several methods including (1) a method comprising thermally hydrolyzing a titanium compound such as titanyl sulfate, titanium chloride, titanium alkoxides, and the like, if necessary, in the presence of seeds for nucleation, (2) a method comprising neutralizing a titanium compound such as titanyl sulfate, titanium chloride, titanium alkoxides, and the like, by adding an alkali, if necessary, in the presence of seeds for nucleation, (3) a method comprising oxidizing titanium chloride, titanium alkoxides, and the like in the vapor phase, and (4) a method comprising firing or hydrothermally treating the titanium oxides produced by any one of the methods (1) and (2). Specifically those titanium oxides obtained by the method (1) or by the hydrothermal treatment at temperatures of 100°C

or higher are preferred because of their higher photocatalytic function. As used in the present invention, the term "titanium oxides" is meant to indicate those so-called hydrated titanium oxide, hydrous titanium oxide, metatitanates, orthotitanates, titanium hydroxide, besides titanium oxide, regardless of their crystal system. In order to allow at least one metal and/or compound thereof selected from the group consisting of V, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Pt and Au as a second component to be present inside the photocatalyst particles and/or on the surfaces thereof, one can employ a method comprising adding the metal and/or the compound to be adsorbed during the production of the photocatalyst particles, or a method comprising adding the metal and/or the compound to be adsorbed after the production of the photocatalyst particles, if necessary, under heat, or if necessary, using reduction.

[0016] The substrates to be used in the present invention include inorganic articles such as ceramics and glasses, organic articles such as plastics, elastomers, woods and paper sheets, and metallic articles made of a metal such as aluminum or an alloy such as steel. Dimensions and forms of the substrates are not critical. Even coated articles may be used.

[0017] In the present invention, it is preferred that both the photocatalyst particles and an adsorbent are adhered onto a substrate via the less degradative adhesive because there coexist an action adsorbing treatment materials. The adsorbents to be used include general adsorbents such as activated carbon, zeolites, silica gels, and the like.

[0018] As already outlined above according to the present invention, a first layer consisting of an adhesive without containing any photocatalyst particles is provided on a substrate, and then a second layer consisting of a less degradative adhesive and photocatalyst particles is provided on the first layer. The provision of the first layer containing no photocatalyst particle enables a firm connection between the substrate and the second layer containing the photocatalyst particles resulting in a firmer adhesion of the photocatalyst particles onto the substrate sustainable for a longer period of time. Moreover, the first layer should preferably contain inorganic particles having no photocatalytic function as filler. Such inorganic particles to be used include those of titanium oxides, silicon oxide, aluminum oxide, magnesium oxide and the like, the surfaces of which are coated with silicon oxide, aluminum oxide, or zirconium oxide.

[0019] The photocatalyst composite according to the present invention may be produced by applying an organic adhesive such as acrylic resins, epoxy resins, polyester resins, melamine resins, urethane resins, alkyd resins and the like, or a less degradative adhesive such as fluorinated polymers, silicone based polymers and the like by coating or spraying onto the substrate to form a first layer and then providing on the first layer the second layer consisting of the photocatalyst particles and the less degradative adhesive by coating or spraying the coating composition on at least a part of said first layer and then fixing the adhesive to adhere the photocatalyst particles onto the substrate via the adhesive. The organic adhesive may be of such a kind as normally used. The silicon based polymers to be used include linear silicone resins, acryl modified silicone resins, various silicone elastomers, and the like. In the present invention, specifically the photocatalyst particles and the less degradative adhesive should preferably be dispersed in a solvent to prepare a coating composition which is then coated or sprayed on a substrate to dispose the photocatalyst particles and the less degradative adhesive on at least a part of the substrate. The solvents to be used include water, and organic solvents such as toluene, alcohols, and the like. The less degradative adhesives to be contained in the coating composition include the aforementioned ones which should preferably be soluble to the solvents used. In the present invention, the less degradative adhesive contained in the coating composition is one or more polymers selected from the group consisting of a fluorinated polymer. The amount of the photocatalyst particles is in the range of 5 to 98 % by volume, preferably 20 to 98 % by volume, more preferably 50 to 98 % by volume, and most preferably 70 to 98 % by volume, based on the total amount of the photocatalyst particles and the less degradative adhesive. The coating compositions may be formulated with cross linking agents, dispersants and fillers. The cross linking agents to be used include ordinary ones of isocyanate family and melamine family and the dispersants to be used include coupling agents. Particularly when the content of the photocatalyst particles in the coating composition is in the range of 40 to 98 % by volume based on the total amount of the photocatalyst particles and the less degradative adhesive, it is preferred to formulate the coating composition with a coupling agent. The amount of the coupling agents to be added should be preferably from 5 to 50 %, more preferably 7 to 30 %.

[0020] The application of the each coating composition may be accomplished by coating or spraying according to any one of ordinary coating techniques including immersing, dip-coating, spin-coating, blade coating, roller coating, wire bar coating, reversal roll coating, or an ordinary spraying technique such as spray coating to dispose the photocatalyst particles and the less degradative adhesive on at least a part of the substrate provided with the first layer.

[0021] After coating or spraying, the composition is fixed to produce the photocatalyst composite of the present invention. The fixation may be performed by a technique of drying, irradiating with ultraviolet rays, heating, cooling, or using a cross linking agent and it is achieved at a temperature lower than 400 °C, preferably from room temperature to 200 °C. In this regard, a temperature higher than 400 °C may undesirably cause thermal degradation of the adhesive rendering the photocatalyst particles readily releasable. The present invention prefers to employ a method for fixation with cross linking agents of isocyanate family and melamine family.

[0022] The photocatalyst composite according to the present invention can cause purification and sterilization of products containing deleterious materials, malodorous materials and oily materials as well as decomposition of such

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materials which come into the vicinity of the photocatalyst particles by irradiating with a ray having a wavelength corresponding to not less than the band gap energy. The radiations to be used for the exposure include light rays including ultraviolet rays, for example, the sun's rays, and lights from fluorescent lamp, black lamp, halogen lamp, xenon flash lamp, mercury lamp and the like. Particularly the light rays including near ultraviolet rays of 300 to 400 nm are preferred.

The intensity and the time of irradiation with the light rays can be determined routinely depending upon the amounts of materials to be treated.

[0023] The present invention will be illustrated below with reference to the following example.

Example

[0024] To an acidic titania sol obtained by thermal hydrolysis of titanyl sulfate (CS-N, available from Ishihara Sangyo Kaisha, Ltd.), there was added sodium hydroxide to adjust the pH to 7, followed by filtration and washing. Then, to the resulting titanium oxide wet cake was added water to prepare a slurry of 100 grams/liter expressed as TiO_2 .

[0025] Sodium hydroxide was added to this slurry to adjust the pH to 10, and then hydrothermal treatment was conducted in an autoclave at a temperature of 150 °C for 3 hours. Then the slurry after the hydrothermal treatment was neutralized to pH 7 by adding nitric acid, filtered, and washed with water, followed by drying at a temperature of 110 °C for 3 hours to yield titanium oxides.

[0026] Then a mixture of the composition indicated below was shaken in a paint shaker for 3 hours to effect sufficient mixing, and dispersed to produce a coating composition (A). The LUMIFRON LF 200C as referred to below is a fluorinated polymer comprising primarily a copolymer of vinyl ether and fluoroolefin.

Titanium oxides (with photocatalytic function)	9.80 grams
Fluorinated polymer (LUMIFRON LF200C, available from Asahi Glass Co., Ltd.)	0.80 gram
Isocyanate based curing agent	0.16 gram
Titanium coupling agent (PLANEACT 338X, available from Ajinomoto Co., Inc.)	1.00 gram
Toluene	23.60 ml

[0027] Then a mixture of the composition indicated below was shaken in a paint shaker for 1 hour to effect sufficient mixing, and dispersed to produce a coating composition (B).

Titanium oxides (having no photocatalytic function) (CR-90, available from Ishihara Sangyo Kaisha, Ltd.)	3.3 grams
Fluorinated polymer (LUMIFRON LF200C, available from Asahi Glass Co., Ltd.)	5.5 grams
Isocyanate based curing agent	1.1 grams
Toluene	20.7 ml

[0028] The latter coating composition (B) was all coated on a transparent acrylic plate by means of a spin coater (1000 r.p.m. x 10 sec) to provide the transparent acrylic plate on the surface thereof with a first layer consisting of the less degradative adhesive and inorganic particles without any photocatalytic activity. Said acrylic plate was used as a substrate.

[0029] Finally the former coating composition (A) was coated onto said acrylic plate substrate and dried at a temperature of 120 °C for 20 minutes to produce a photocatalyst of the present invention (Sample F). The content of titanium oxides, i.e. the photocatalyst particles in the second layer, of this Sample F was 90 % by volume based on the total amount of the titanium oxides and the less degradative adhesive.

[0030] Measurements of the weight loss of the adhesive used for Sample F in the procedure that Sample F was exposed to the black light at an ultraviolet intensity of 7 mW/cm² on the surface of Sample F for 5 hours revealed that there was found no weight change in Sample F of the present invention, and the adhesive was not degraded and the titanium oxide photocatalyst particles were not released from the substrate. The film strength, of Sample F of this Example was 3H in terms of pencil hardness, which means that the photocatalyst particles were firmly adhered. Furthermore, the Sample F was placed in a flow of water and irradiated with the black light in such a manner that the superficial ultraviolet intensity was 2 mW/cm² for 3 weeks. However, there was observed no releasing of the titanium oxide photocatalyst particles from the substrate.

[0031] The photocatalyst composite of the present invention comprises a substrate having photocatalyst particles thereon via a less degradative adhesive, and causes very little decomposition and degradation of the adhesive owing to the photocatalytic function. The present invention enables long-term firm adhesion of photocatalyst particles onto any substrate without damaging the photocatalytic function. The utilization of the photocatalyst composite of the

present invention allows effective and prompt removal of deleterious materials, malodorous materials, oily components, bacteria, actinomyces, fungi, algae and the like. Therefore, the photocatalyst composite is very useful as deodorant and sterilizer both at home and in industry. In addition, the photocatalyst composite of the present invention can be used for an extended period of time, has a high degree of safety, finds applicability to a wide variety of deleterious materials, and is disposable without polluting the environment. Thus, it is very useful in industry. In the process for producing the photocatalyst composite according to the present invention, the use of fluorinated polymers as less degradative adhesives enables production of preferred photocatalyst composites, the surfaces of which have a lesser tendency to adsorb dust and contaminants due to weak sticking power of the fluorinated polymers.

[0032] The process for producing the photocatalyst composite according to the present invention is a useful process which can employ any materials such as plastics as substrate and produce conveniently and easily consistent quality photocatalyst composites.

[0033] The coating composition of the present invention can be coated or sprayed onto substrates of any form or desired sites thereof, and allows the ready utilizing of the photocatalytic function. Thus, particularly it is useful for domestic applications.

Claims

1. A photocatalyst composite comprising a substrate having photocatalyst particles adhered thereon via a less degradative adhesive wherein on the substrate is provided a first layer comprising an adhesive without containing any photocatalyst particles and further on said first layer is provided a second layer comprising the less degradative adhesive and the photocatalyst particles, said less degradative adhesive being one or more polymers selected from the group consisting of a fluorinated polymer.
2. The photocatalyst composite according to claim 1, wherein said photocatalyst particles and an adsorbent are adhered to the substrate via said less degradative adhesive.
3. The photocatalyst composite according to claim 1, wherein the adhesive of said first layer is a less degradative adhesive.
4. The photocatalyst composite according to claim 1, wherein said first layer consists of a less degradative adhesive and inorganic particles.
5. The photocatalyst composite according to claim 1, wherein said photocatalyst particles are of titanium oxide.
6. The photocatalyst composite according to claim 1, wherein said photocatalyst particles contain at least one selected from the group consisting of metals and metal compounds of V, Fe, Co, Ni, Cu, Zn, Ru, Rh, Pd, Ag, Pt and Au as a second component inside said photocatalyst particles and/or on the surfaces thereof.
7. A process for producing a photocatalyst composite by disposing photocatalyst particles and an adhesive on a substrate and then solidifying the adhesive to adhere the photocatalyst particles via the adhesive, said process also comprising the steps of providing a first layer of an adhesive free from photocatalyst particles on a substrate by coating or spraying said substrate with said adhesive and fixing said adhesive onto said substrate, and then providing a second layer comprising a less degradative adhesive and the photocatalyst particles on said first layer and then fixing said adhesive and photocatalyst particles on said first layer, said less degradative adhesive being one or more polymers selected from the group consisting of a fluorinated polymer.
8. A coating composition characterized by comprising a dispersion of photocatalyst particles and a less degradative adhesive in a solvent, said adhesive being one or more polymers selected from the group consisting of a fluorinated polymer.
9. The coating composition according to claim 8, comprising a dispersion of the photocatalyst particles, a less degradative adhesive and a coupling agent in a solvent.



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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (InCL17)
A	DATABASE WPI Section Ch, Week 9247 Derwent Publications Ltd., London, GB; Class A14, AN 92-386090 XP002073751 & JP 04 284851 A (JAPAN STORAGE BATTERY CO LTD) * abstract *	1	801J35/00
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The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (InCL17) B01J
Place of search THE HAGUE		Date of completion of the search 18 September 2001	Examiner Thion, M
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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